Welcome!!

Chemistry 328N- 50120

Organic Chemistry for Chemical Engineers

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http://willson.cm.utexas.edu

Bureaucracy:

- Please read the syllabus carefully
- Homework Instructions will be provided on Thursday
- Attend all lectures
- Do the homework
- ***Don't get behind***
- Take advantage of office hours
  - We want to get to know you
- Watch the web page
  - http://willson.cm.utexas.edu (teaching)
- *Keep up with the work!*
- *You can't "cram" for the exams in this class*
- ***Don't get behind!!***

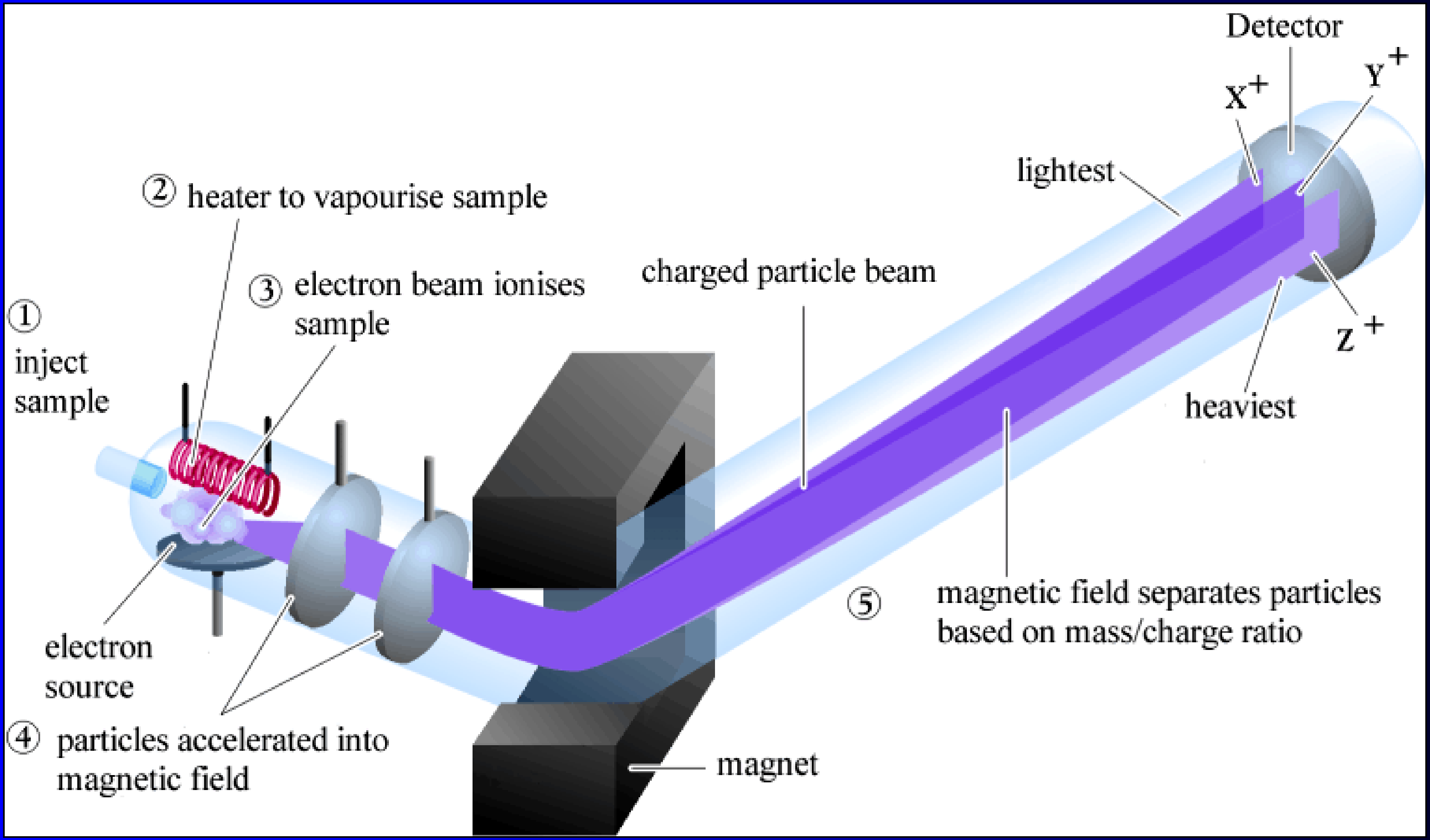
Homework..

- A detailed procedure for turning in and picking up homework will be provided on Thursday.
- There are problems assigned from the text book and there are “supplemental” problems.
- Answers to the problems from the text are provided in the Study Guide for the eighth edition of the text book.
- Answers to the supplemental problems will be posted on the web site.

Structure Determination

- We will spend some time learning how to establish the structure of “unknown” organic compounds through use of spectroscopic analysis.
  - Mass spectroscopy
  - Nuclear Magnetic Resonance Spectroscopy
  - Infrared spectroscopy
  - UV-Visible Spectroscopy

Mass Spectrometer



A Mass Spectrometer

- A mass spectrometer is designed to do three things:

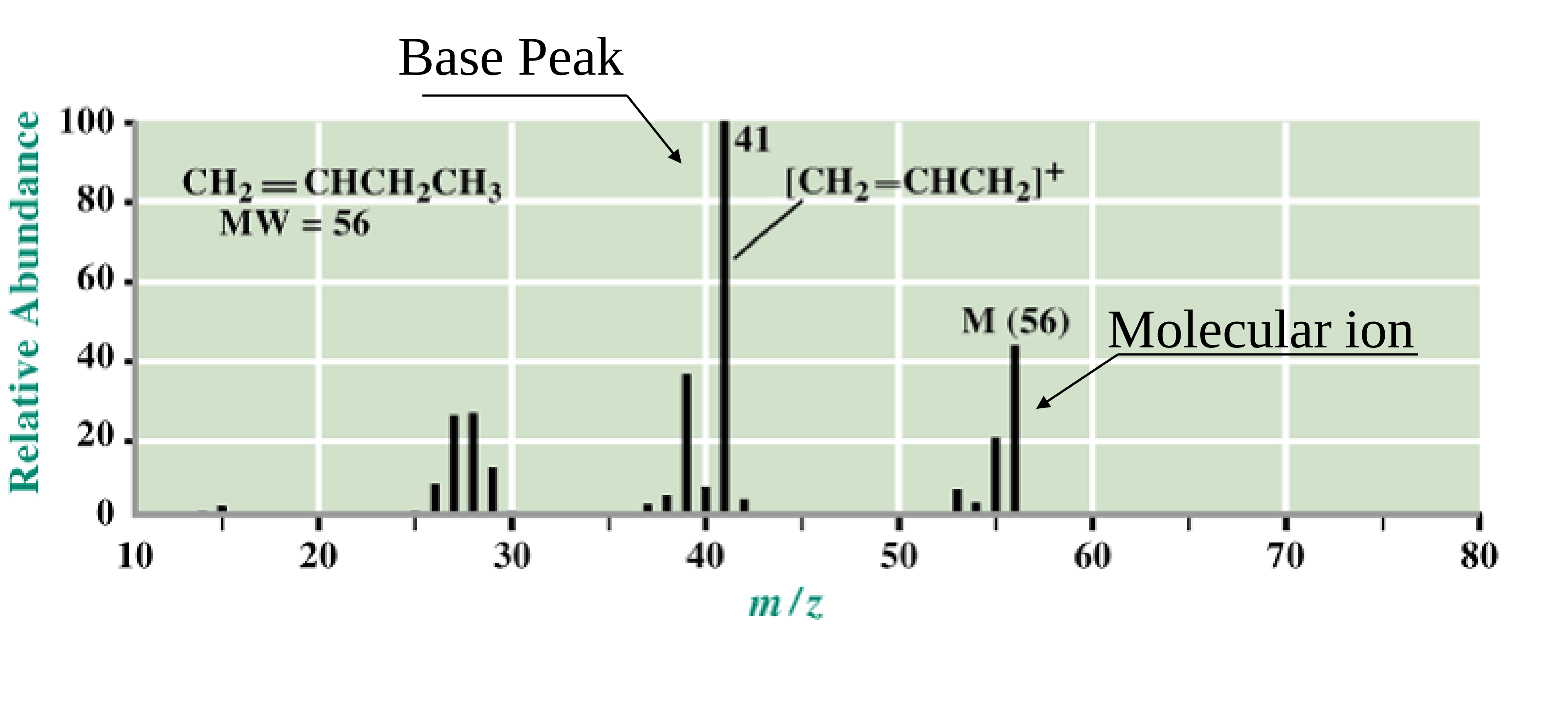
1. Convert neutral atoms or molecules into a beam of positive (or negative) ions

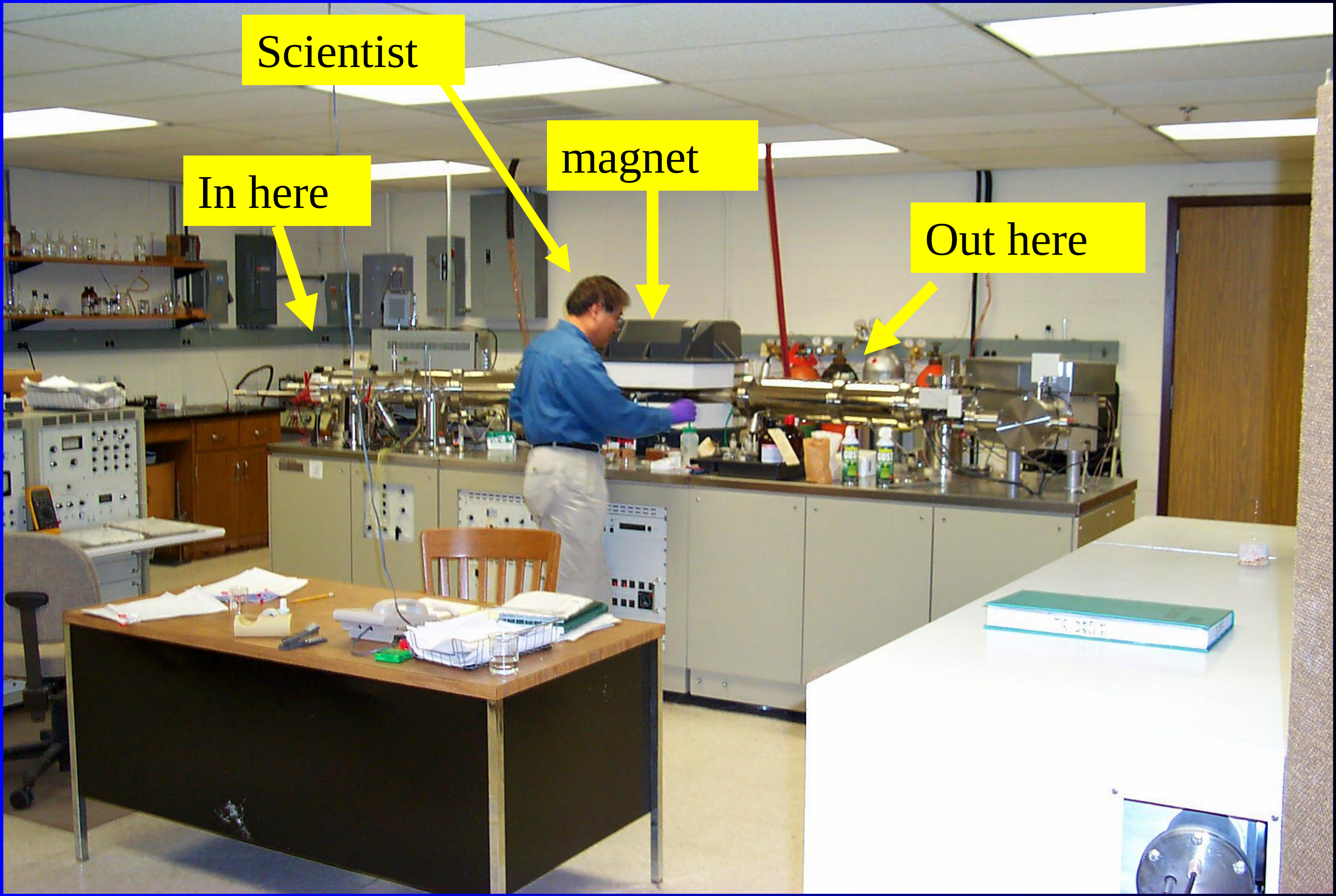
2. Separate the ions on the basis of their mass-to-charge ratio (m/z)

3. Measure the relative abundance of each ion

https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/spectrpy/massspec/masspec1.htm

Mass Spectrum




Scientist
magnet
In here
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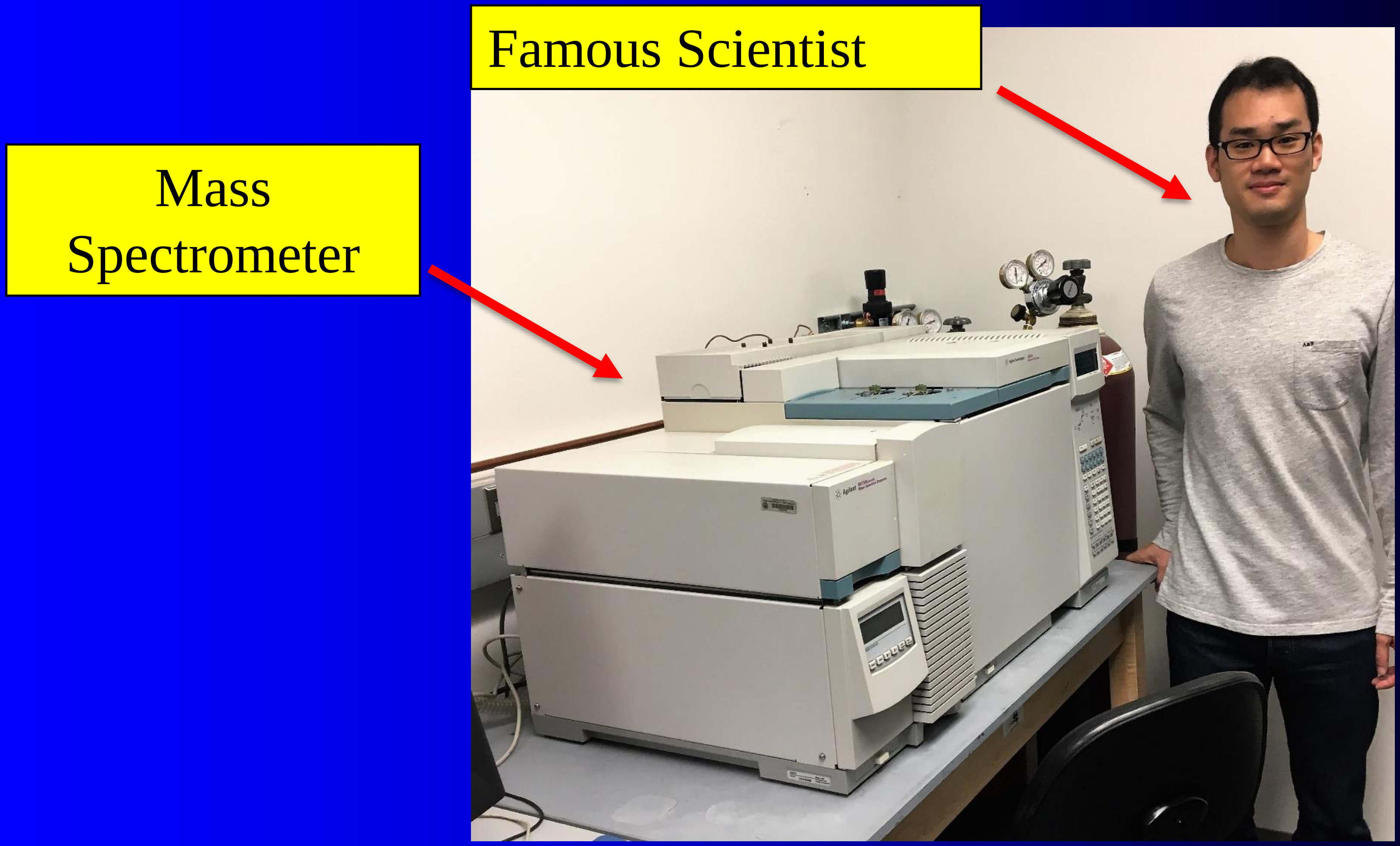
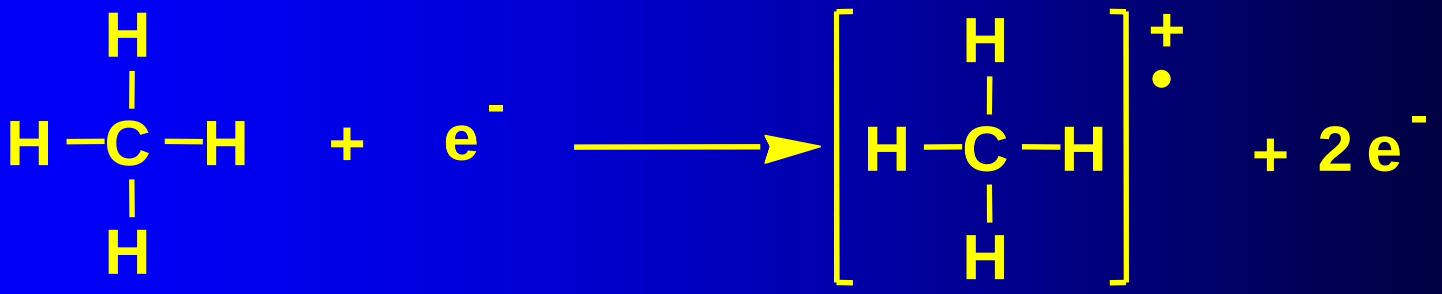
Modern Mass Spectrometer

unit mass resolution



A Mass Spectrometer

- Electron ionization MS
  - In the ionization chamber, the sample is bombarded with a beam of high-energy electrons
  - Collisions between these electrons and the sample result in loss of electrons from sample molecules and formation of positive ions



Molecular ion
(A radical cation)

Molecular Ion

- Molecular ion (M or M^+): the species formed by removal of a single electron from a molecule

- For our purposes, it does not matter which electron is lost; radical cation character is delocalized throughout the molecule. Therefore, we write the molecular formula of the parent molecule in brackets with
  - A plus sign to show that it is a cation
  - A dot to show that it has an odd number of electrons

$$[CH_3CH_2OCH_3]^{+\bullet}$$

Molecular Ion

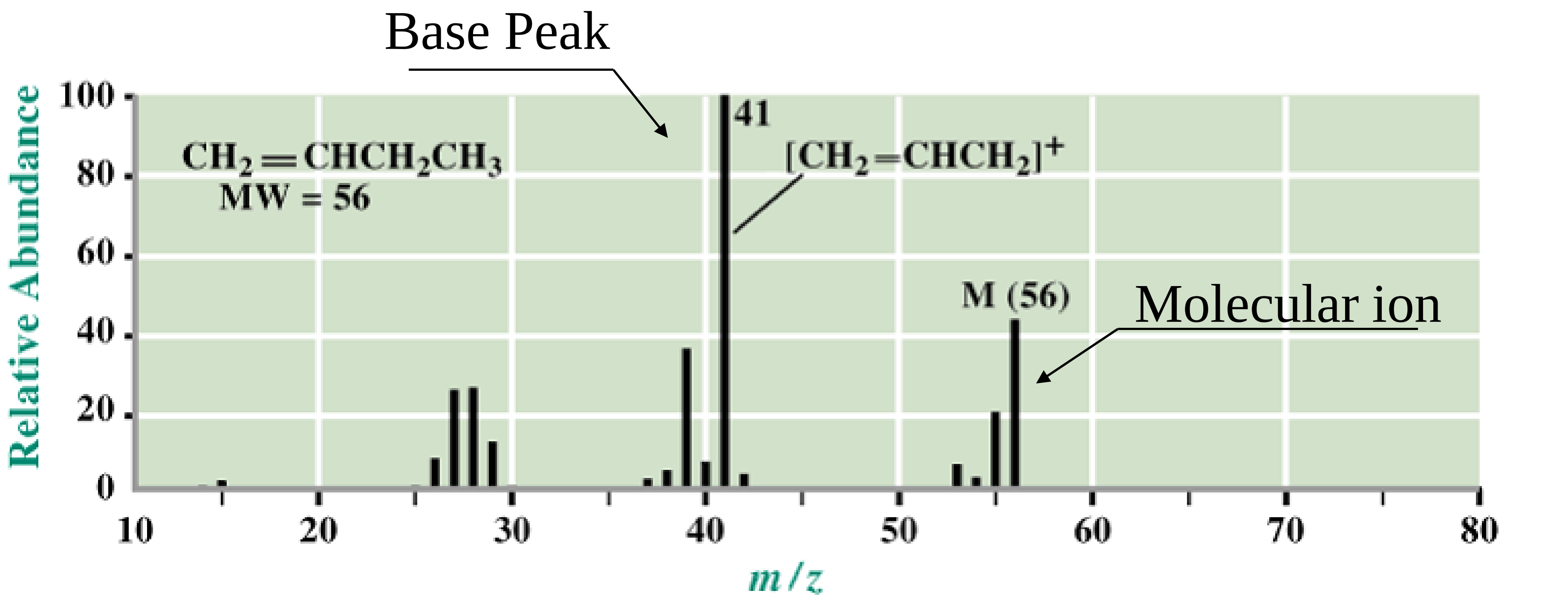
- At times, however, we find it useful to depict the radical cation at a certain position in order to better understand its reactions

$$[CH_3CH_2OCH(CH_3)_2]^{+\bullet} \qquad [CH_3CH_2\ddot{\dot{O}}CH(CH_3)_2]^{+}$$

Mass Spectrum

- Mass spectrum: a plot of the relative abundance of each ion versus mass-to-charge ratio
- Base peak: the most abundant peak; assigned an arbitrary intensity of 100
- The relative abundance of all other ions is reported as a % of abundance of the base peak

Mass Spectrum of 1-Butene



The Nitrogen Rule

- Nitrogen rule: if a compound has
  - zero or an even number of nitrogen atoms, its molecular ion will have an *even* m/z value
  - an odd number of nitrogen atoms, the molecular ion will have an *odd* m/z value

Other MS Techniques

- What we have described is called electron ionization mass spectrometry (EI MS)

- Other techniques include
  - Fast atom bombardment (FAB)
  - Matrix assisted laser desorption ionization (MALDI)
  - Chemical ionization (CI)
  - And many others….

Resolution

- Resolution: a measure of how well a mass spectrometer separates ions of different mass
  - Low resolution - capable of distinguishing among ions of different nominal mass, that is ions that differ by at least one or more atomic mass units (Daltons)
  - High resolution - capable of distinguishing among ions that differ in mass by as little as 0.0001 mass units

High Resolution Mass Spectrometer

Resolution

- **C_3H_6O and C_3H_8O have nominal masses of 58 and 60 respectively, and can be readily distinguished by low-resolution MS**

- **$C_2H_4O_2$ and C_3H_8O** both have a nominal mass of 60. However, we can still distinguish between them by high-resolution MS

Molecular Formula	Nominal Mass	Precise Mass
C_3H_8O	60	60.05754
$C_2H_4O_2$	60	60.02112

Differences are due to Isotopes

- In nature Carbon is 98.90% ^{12}C and 1.10% ^{13}C. Thus, there are 1.11 atoms of carbon-13 in nature for every 100 atoms of carbon-12…Mass spectroscopists use this measure rather than %!!!!!!

$$\left[\frac{1.10\ ^{13}C}{98.90\ ^{12}C} \right] \times 100\ ^{12}C \text{ atoms} = 1.11\ ^{13}C \text{ per } 100\ ^{12}C$$

- The **“ relative abundance”** of ^{13}C is defined as 1.11

Precise masses and natural abundances of isotopes

Element	Atomic Weight	Isotope	Precise Mass (amu)	Relative Abundance
hydrogen	1.0079	^{1}H	1.00783	100
		^{2}H	2.01410	0.016
carbon	12.011	^{12}C	12.0000	100
		^{13}C	13.0034	1.11
nitrogen	14.007	^{14}N	14.0031	100
		^{15}N	15.0001	0.38
oxygen	15.999	^{16}O	15.9949	100
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
sulfur	32.066	^{32}S	31.9721	100
		^{33}S	32.9715	0.78
		^{34}S	33.9679	4.40
chlorine	35.453	^{35}Cl	34.9689	100
		^{37}Cl	36.9659	32.5
bromine	79.904	^{79}Br	78.9183	100
		^{81}Br	80.9163	98.0

Calculation of Precise Mass

Use mass of most abundant isotope…why??

C_3H_8O and $C_2H_4O_2$

C	12	3	36	2	24
H	1.00783	8	8.06264	4	4.03132
O	15.9949	1	15.9949	2	31.9898
SUM			60.05754		60.02112

http://www.colby.edu/chemistry/NMR/IsoClus.html